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Dielectric studies of gel grown zinc tartrate crystals

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Abstract : Zinc dextro tartrate and zinc levo tartrate crystals were grown by using optically sensitive dextro tartaric acid and levo tartaric acid, respectively. These crystals were grown by a single diffusion gel growth technique using silica hydro gel. The variation in dielectric constant and loss tangent values, for both zinc dextro tartrate and zinc levo tartrate crystalline samples, was measured at different temperatures in the frequency range from 5 kHz to 1 MHz. A sharp peak was observed in the dielectric constant *versus* temperature plots at 121.52 °C indicating a phase transition. Beyond this temperature, the Curie- Weiss law was found to be followed The variation of the dielectric constant with frequency was also studied. The results are discussed.

Keywords Zinc tartrate, spherulitic crystals, dielectric behaviour, tangent loss, Curie- Weiss plot, gel growth

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1. Introduction

In the recent years, due to various applications, the dielectric behaviour of various tartrate compounds has fetched significant importance. Moreover, the ferro-electricity was observed in tartrate compounds by many authors, for example, in sodium-potassium tartrate crystals as early as in 1921 by Valasek [1], calcium tartrate [2], sodium- ammonium tartrate [3]. Recently, strontium tartrate trihydrate is identified for pyroelectric and ferroelectric transitions, which can have some device applications [4].

Zinc tartrate is a quite interesting compound, and hence some attempts had been made to grow its crystals. However, an earlier attempt was made by Henisch *et al* [5] in 1965 to grow zinc tartrate crystals by a gel technique; later on in 1995, Lopez *et al* [6] have grown zinc tartrate crystals. Many important applications of zinc tartrate compounds have been identified such as, the synergist in cosmetic materials [7], in protecting powder for metals [8], in phosphorescence [9]. Altogether, this has attracted present authors to grow zinc tartrate crystals using optically sensitive dextro tartaric acid and levo tartaric acid in a silica hydro gel medium and to study their dielectric behaviour at different temperatures and frequencies in order to identify the presence of any phase transition, and also to know whether the effect of optically sensitive tartrate radicals are present or not.

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2. Experimental techniques

The crystallization apparatus employed was a glass test tube of 25 mm diameter and 140 mm length. The AR grade chemicals were used to grow the crystals. The gel was prepared by mixing 1M dextro tartaric acid or 1M levo tartaric acid solutions with sodium metasilicate solution of appropriate specific gravity so that the desired pH of the mixture could be obtained. The specific gravity and pH were varied between 1.02 to 1.05 and 4.0 to 5.0, respectively. After setting the gel, the feed solution of 1M $ZnCl_2$ was poured without disturbing the gel surface. The nucleation was observed within 24 h and spherulitic crystals were grown in a month having maximum diameter of 0.56 cm. The spherulites were found to be semi-transparent, light brown in color, with small spiky and faceted growth on their surfaces. Good quality crystals were grown for pH 4.5 and specific gravity 1.04. Figure 1 is a photograph of zinc dextro tartrate crystals at specific gravity 1.04 and pH 4.5. The following reaction is expected to occur during the process.

$$ZnCl_2\ nH_2O + H_2C_4H_4O_6 \rightarrow ZnC_4H_4O_6\ mH_2O + 2HCl + (n\text{-}m)\ H_2O\ (n > m).$$

The confirmation of the crystal formation was done by carrying out FTIR spectroscopy, TGA, Powder XRD and EDAX. As the crystals had spherulitic morphology, they could not be

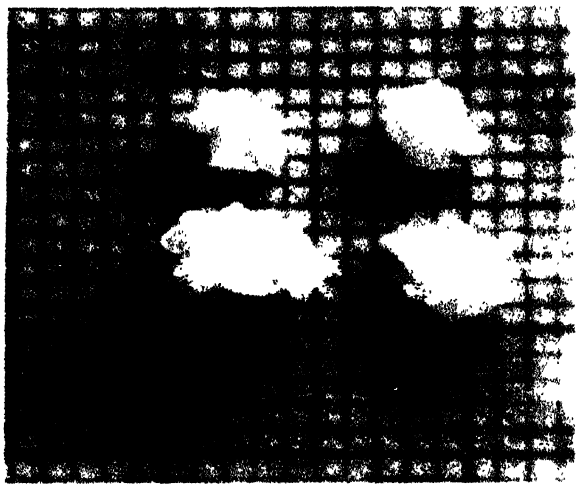

Figure 1. Typical semi-transparent, light brown color, spiky, faceted, spherulitic, crystals of zinc dextro and zinc levo tartrates

placed in the sample holder directly. Therefore, crystals were powdered in a conventional way and palletized into 1 cm diameter using a hydraulic press at the pressure of 2×10^6 N/m^2. Acetone was used as binders. A specially designed sample holder was used, which can be kept in a resistance heated muffle furnace for measurements at different temperatures [4, 10]. The sample temperature was monitored using a chromel-alumel thermocouple (± 1°C). The temperature was raised by regulating the input power through 15 A dimmerstat.

In the present study, the variation of capacitance and loss tangent (tan δ) of pallet samples is reported for temperature and frequency ranges from 25 °C to 233 °C and 5 kHz to 1MHz, respectively. The capacitance measurement was carried out using a precision LCR meter (Hewlett Packard 4284 A). The value of dielectric constant was calculated by using the following formula,

$$C = \varepsilon A / t = \varepsilon_0\ \kappa\ A / t, \quad \kappa = Ct / \varepsilon_0 A,$$

Where C = capacitance, ε = relative permittivity, A = area of sample, ε_0 = permittivity of free space and κ = dielectric constant.

3. Results and discussion

Gon [2] studied dielectric behaviour of calcium tartrate single crystal and reported its ferroelectric properties. The variation of dielectric constant (κ) with temperature for different frequencies showed sharp peak at 123°C. The variation of κ and tanδ with frequency exhibited decrease in the values of κ and tanδ with increase in frequency, and then remain almost constant. Th peak value of dielectric constant decreases with increasin frequency. Gon [2] also obtained the Curie-Weiss plot for calciu tartrate crystals just after the peak temperature and confirme the ferroelectric behaviour through the hysteresis loop, where the behaviour of dielectric constant of potassium-sodiu tartrate with temperature has been studied in the microwav region by Denda [11]. The dielectric study of zinc tartrate w reported by Lopez *et al* [6]. They studied the variation of dielectr constant and loss tangent with frequency. They did not stud the variations of dielectric constant as well as the loss tange with temperature. Recently, the dielectric behaviour of strontiu tartrate trihydrate (STT) single crystals has been studied b Arora *et al* [4]. The dielectric constant and loss tange exhibit similar trend of variation in the plots with frequency a well as with temperature. The same authors have reporte pyro-electric and possible ferroelectric behaviours of STT singl crystals.

Various crystals exhibit different interesting phases in the dielectric properties. Sodium potassium niobate system exhibi property such as, a number of ferroelectric phases with hig spontaneous polarization, low dielectric constant and hig electromechanical coupling coefficient. The dielectric propertie of $Na_{1-x}K_xNbO_3$ crystals in orthorhombic phase have bee reported by Lingwal *et al* [12]. Apart from this, Mohankumar *et al* [13] reported the ferroelectric and pyroelectric properties triglycine sulphate single crystals in the presence of variou doping. The doping has pronounced effect on the Curi temperature, spontaneous polarization and coercive field

In the present investigation, an attempt has been made t study the dielectric properties of both dextro and levo tartrat crystals of zinc, and to find out if the difference is there in thei properties. Figure 2 exhibits the variation of dielectric constan

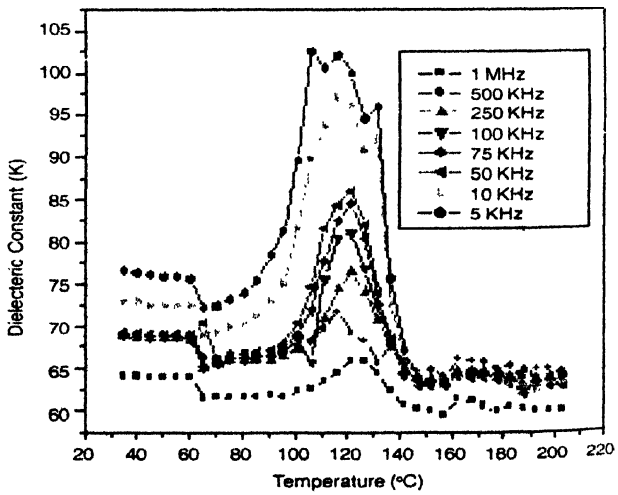

Figure 2. Dielectric constant (κ) *versus* temperature for differen frequencies for zinc dextro tartrate.

with temperature at different frequencies for zinc dextro tartrate crystals. It can be noticed, that a sudden transition in the values of dielectric constant has taken place at 65.64 ^{0}C, which may be due to onset of dehydration and removal of H^+ and OH^- ions from the sample. This can be confirmed by the thermogram of zinc dextro tartrate crystals, which is discussed in details for zinc dextro and zinc levo tartrate crystals by Dabhi and Joshi [14], where the crystals start decomposing at 60 ^{0}C, and at 120 ^{0}C become anhydrous. In all plots, the value of sharp peak is observed at 121.52 ^{0}C, which may be due to phase transition. Due to the experimental limitations, the present authors could not perform the hysterisis loop measurements; hence the phase transition could not be confirmed. An abnormality was observed at 5 kHz and lower frequencies up to 500 Hz, that the sharp peak got some flattened and scattered points. Mansingh and Bawa [15] observed this type of abnormality in the potassium ferrocyanide trihydrate compressed powder and explained the phase transition on the basis of particle size and packing fraction. The measurements by reversing the temperature cycle were not carried out since the crystal begins to undergo thermal phase transition.

Figure 3 exhibits the variation of dielectric constant with temperature at different frequencies for zinc levo tartrate crystals. In all plots, the peak value of dielectric constant is occurring at 121.52 ^{0}C, which may again be regarded as the phase transition temperature. Unlike the zinc dextro tartrate crystals, no sudden decrease in the dielectric constant at 65.64 ^{0}C was observed. From Figure 3, one can notice that on heating the sample from room temperature, the values of dielectric constant decrease gradually with temperature, and become minimum at 75.8 ^{0}C; thereafter, again increase with temperature with a peak at 121.52 ^{0}C. The minimum value of dielectric constant at 75.8 ^{0}C is due to dehydration of the crystals, which is occurring at slightly

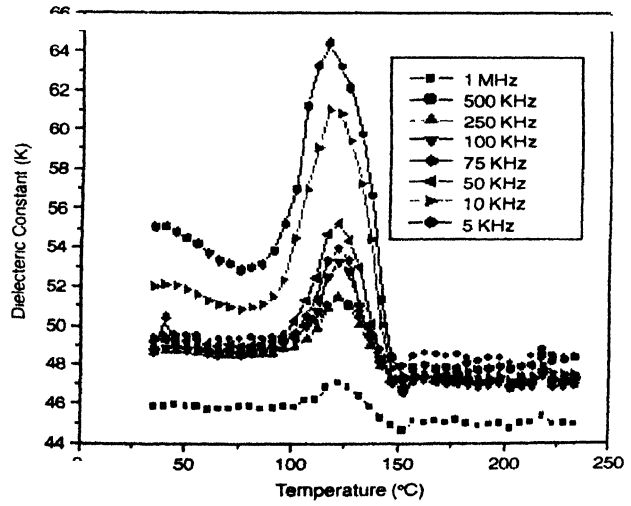

Figure 3. Dielectric constant (κ) *versus* temperature for different frequencies for zinc levo tartrate.

different temperature compared to that of zinc dextro tartrate crystals.

The variation of the peak values of dielectric constants with frequency is displayed in Figure 4 for zinc dextro tartrate. The peak value of κ_p decreases as frequency increases. The same behaviour is observed in the case of zinc levo tartrate crystals. These results are consistent to those of Gon [2] for ferroelectric calcium tartrate single crystals.

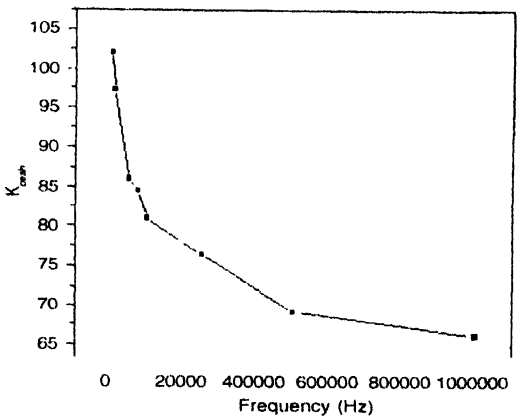

Figure 4. Dielectric constant (κ_p) *versus* frequency for zinc dextro tartrate

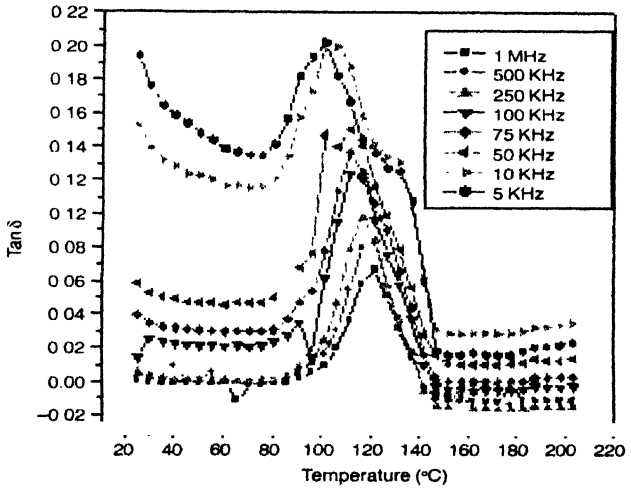

Figure 5. Plot of tanδ *versus* temperature for different frequencies for zinc dextro tartrate.

The variation of tanδ with temperature at different frequency is displayed in Figure 5 for a zinc dextro tartrate crystal. The nature of variation of tanδ with temperature is similar to that of dielectric constant with temperature; here also, one observes tanδ peak at 121.52 ^{0}C. This peak value of tanδ shifts towards the lower temperature side and transforms into a hump. This nature also corresponds to the abnormality observed in the dielectric constant *versus* temperature curve. One also finds a

minimum value occurring at 65.64 °C and a sharp transition towards lower values of tanδ occurring at 141.84 °C. However, the change in the nature of the peak is believed to be due to the compressed powder nature of the samples. The variation of loss-tangent (tanδ) with temperature is shown in Figure 6 for zinc levo tartrate crystals. Studies of the dielectric constant and loss tangent as a function of temperature are used to detect structural and phase transition in crystalline materials. These parameters undergo remarkable change at transition temperature; therefore, it is quite common to study the behaviour of these parameters at different applied frequency.

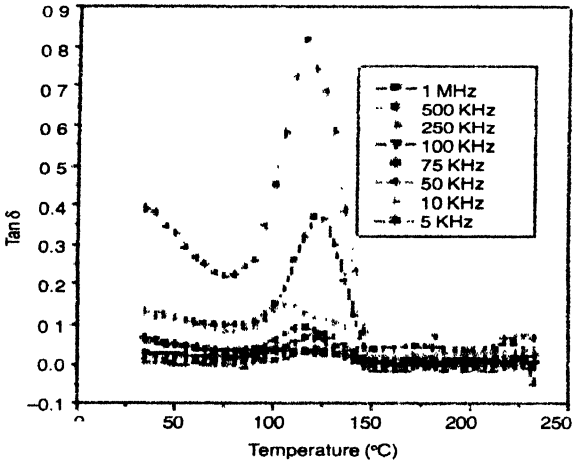

Figure 6. Plots of tanδ *versus* temperature for different frequencies for zinc levo tartrate

The variation of dielectric constant with frequency was studied for both crystals. Figure 7 shows the plots of dielectric constant *versus* log f at various temperatures. It can be seen from these plots that in general, the values of dielectric constant decrease with frequency. Initially, the dielectric constant decreases rapidly with increasing frequency and becomes almost constant in the mid-frequency region and, finally in high frequency region, it again decreases. In general, the variation of dielectric constant with frequency suggests the presence of higher space charge polarizability of the material in the low frequency region. This nature may be explained on the basis of the mechanism of polarization similar to that of conduction process. The electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of applied field, which gives the polarization. As the frequency increases, a point is reached where the space charge cannot sustain and comply with the external field. Therefore, the polarization decreases and exhibits the reduction in the value of dielectric constant as the frequency increases [4]. This behaviour is similar to the nature reported by Lopez *et al* [6] for zinc tartrate crystal at room temperature. The similar nature of the plots is obtained for zinc levo tartrate crystals. Apart from this, Gon [2] suggested that the decrease in the values of dielectric constant as the frequency increases is due to different sizes of domain. This behavior is similar in both zinc dextro and levo tartrate crystals. However, a marked difference was found in the behaviour of copper dextro tartrate and copper levo tartrate crystals by Dabhi [10]. Copper dextro tartrate and copper levo tartrate crystals exhibited different behaviour, which were explained by the author on the basis of the structural change in the presence of dextro tartrate and levo tartrate ions.

Above the Curie temperature, the substance is in the para electric state and found to obey the Curie- Weiss law as $\kappa = C/T - T_c$, where C is the constant and T_c is the Curie temperature. Alternatively, the Curie- Weiss law can be represented by using the susceptibility $\chi = (\kappa - 1)/4\pi$, as follows $1/(\kappa - 1) = T - T_c/C$ [4,16]. Figures 8 and 9 are the Curie Weiss plots, which show relation between $1/(\kappa - 1)$ and $T - T_c$ for zinc dextro tartrate and levo tartrate samples, respectively, at 1 MHz. The linear regression analysis suggests that the Curie Weiss law is followed, just beyond the peak temperature, for

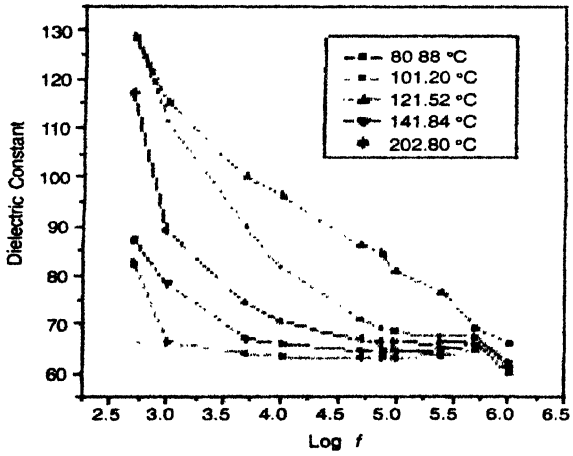

Figure 7. Dielectric constant (κ) *versus* frequency plots for different temperatures for zinc dextro tartrate.

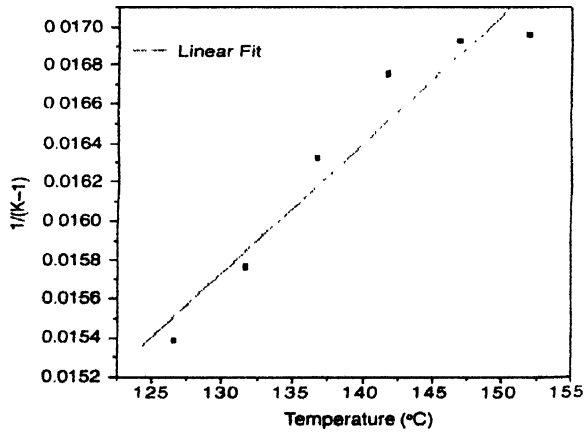

Figure 8. Plot of $(1/\kappa - 1)$ *versus* $(T - T_c)$ for 1MHz frequency for zinc dextro tartrate.

both the crystals with correlation coefficient r-values as 0.9932 and 0.96286 for the Figures 8 and 9, respectively.

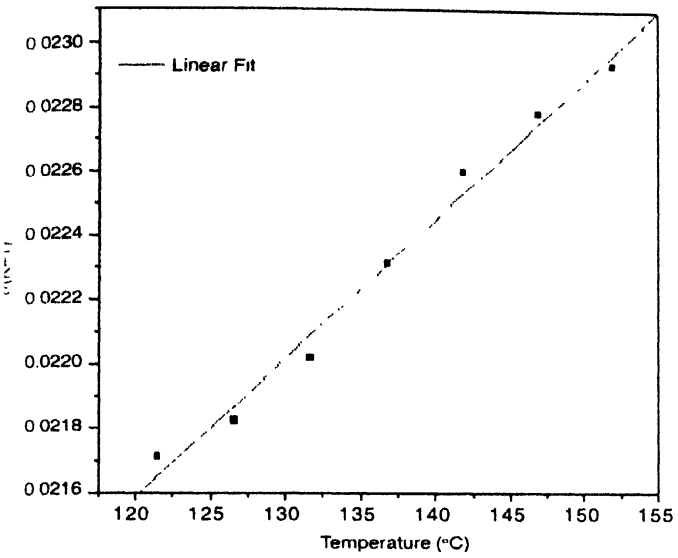

Figure 9. Plot of $(1/\kappa - 1)$ *versus* $(T - T_c)$ for 1MHz frequency for zinc levo tartrate.

Earlier, the thermal studies of gel-grown dextro and levo tartrates of zinc have shown marked difference in the values of activation energy and enthalpy of activation, which was believed to be due to different optically sensitive acids used to grow the crystals [14]. However, in the present study, no clear effect of optically sensitive tartaric acid is found. The crystals are grown in spherulitic form, which is not a single crystalline form. Therefore, instead of using it in as grown form, it is suitable to powder the samples and palletize them so that it can conveniently be placed in the sample holder. In the present study, the hysteresis loop measurements can not be taken due to experimental limitations as well as the crystals exhibit thermal phase transition. Therefore, no temperature reversal data are obtained. This suggests that the ferroelectric to paraelectric transition cannot be confirmed directly from the results of the present investigation. However, the temperature-dependence of dielectric constant and dielectric loss manifests pyro-electric behaviour of the sample.

4. Conclusion

The variation of dielectric constant with temperature indicates a sharp peak at 121.52 ^{0}C for both dextro and levo tartrates of zinc. The variation of loss tangent with temperature exhibits the similar behaviour for both types of samples. The variation of dielectric constant with frequency exhibits that the dielectric constant decreases on increasing the frequency, suggesting higher space charge polarizability in the low frequency region. The gradual decrease in the dielectric constant with the frequency suggests that the sample has domains of different sizes and of various relaxation times, which depends on the temperature of the sample. The peak value of dielectric constant decreases on increasing the frequency suggests that magnitude of the dielectric constant at the phase transition is frequency-dependent. The value of the correlation coefficient of the linear regression analysis is significant and suggests that the Curie-Weiss law is followed. The pyro-electric behaviour is observed, however, a possible ferroelectric to paraelectric transition could not be confirmed due to lack of the data of hysteresis curve. Moreover, no clear effect of the optically sensitive tartaric acid radical is found on the dielectric and possible ferroelectric properties, which was seen earlier in the thermal properties.

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References

[1] J Valasek *Phys. Rev.* **17** 475 (1921)
[2] H B Gon *J. Cryst. Growth* **102** 501 (1990)
[3] K Aizu *J. Phys. Soc. Jpn.* **31** 1521 (1971)
[4] S K Arora, V Patel, B Amin and A Kothari *Bull. Mater Sci.* **27** 141 (2004)
[5] H K Henisch, J Dennis and J J Hanoka *J. Phys. Chem. Solids.* **26** 493 (1965)
[6] T Lopez, J Stockel, J Peraza, M E Torres and A C Yanes *Cryst. Res Technol* **30** 677 (1995)
[7] S Pellaki and Aromi Saponi *Cosmet Aerosol* **48** 31 (1996)
[8] M A Rossi *Italian Patent No 581803*, 9th Sept (1958)
[9] R Iwaki *J. Chem. Soc. Jpn. (Pure Chem. Section).* **76** 605 (1995)
[10] R M Dabhi *Ph.D. Thesis* (Saurashtra University Rajkot) (2002)
[11] H Denda *Z.Naturforsch* **A221**139 (1967)
[12] V Lingwal, B S Semwal and N S Panwar *Bull Mater. Sci* **26** 619 (2003)
[13] R Mohankumar, R Muralidharan, D Rajan Babu, K V Rajendran, R Jayavel, D Jayaraman and P Ramasamy *J. Cryst. Growth* **229** 568 (2001)
[14] R M Dabhi and M J Joshi *Indian J. Phys.* **76A** 211 (2002)
[15] A Mansingh and S S Bawa *Indian J. Pure Appl. Phys.***12** 483 (1974)
[16] A J Dekker, *Solid State Physics* (London: Mac Millan) p193 (1970)